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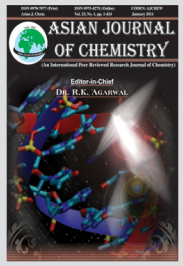

# Quantum Size Effect on Band Gap and Effective Mass of ZnS Nano-Particle

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In this paper, we calculate the band gap of ZnS nanoparticle and show that it increases with decreasing its size. The simplest way for discussing this phenomenon and finding the band gap for different sizes is to use effective mass approximation. We show this method isn't useful for smaller sizes than 2.5 Å because the effective mass of particles below 2.5 Å also depends on the size. The density functional theory was used to obtain the band gap of ZnS nanoparticle. This theory also be used for determine the effective mass for various particle size. We find equation that shown variation effective mass for various particle sizes of ZnS. This equation fit with experimental results.

**Key Words: Band gap, Density functional theory, Effective mass, Nanoparticle.**

## INTRODUCTION

Quantum confinement effects in semiconductor quantum dots (QDs) were discovered more than two decades ago[1] and have attracted more attention during recent years due to their properties of nanoscale quantum confinement[2-4] and the consequent potential for size-tunable nanodevices. They have great promise for a variety of applications in optoelectronics such as optically pumped lasers[5], light emitting diode[6], solar cell[7], biomedicine as chemical markers[8] and in telecommunications[9]. Being a compound semiconductor, ZnS has found many applications in various fields. ZnS nanoparticles can be used as thin film or in the form quantum dots. ZnS quantum dot is of interest as a phosphor and electroluminescent material and is a system in which electrical and structural properties are a function of particle size[10]. In a semiconductor nanoparticle, the size effects appear when the radius of the particle is comparable to the Bohr radius of the exciton in the bulk material. Quantum size effects play an important role for ZnS quantum dots with a diameter in the 1-5 nm[11,12]. These ranges of size cover the transition regime between the bulk and molecule of ZnS. In these sizes reduced number of atoms in the cluster and increased the ratio of number atoms on the surface to the volume. The energy gap in such a situation widens and the energy levels become approximately like molecular levels. The small size of these particles will result in quantum confinement of the photo-generated electron-hole pair, leading to a blue shift in the absorption spectrum[13,14]. As a consequent, by controlling the quantum particle size, we can control optical and transparent properties.

In this paper, the effective mass is calculated for ZnS quantum dots and showed the effective mass changed with its size. A new equation is also shown the variation effective mass for various particle sizes of ZnS. This equation fit with experimental results.

## EXPERIMENTAL

**Effective mass:** There are many methods for study the quantum size effects for nanoparticles[15-17]. Due to the importance of band gap in manufacturing optical devices we have tried to find the band gap of ZnS quantum dots in different sizes. The best and the fastest theoretical techniques calculating band gap in quantum dots is the effective mass approximation (EMA)[1]. The effective mass theory has become an essential ingredient in several branches of modern physics like, nuclear physics[18], solid state physics, such as quantum dots, the description of electronic properties of semiconductors[19] and quantum dots[16], quantum liquids[20], He clusters[21] and metal clusters[22].

The Hamiltonian of quantum dots with used EMA is written by[23]:

$$\hat{H} = \frac{-\hbar^2}{2m_e^*}\nabla_\varepsilon^2 - \frac{-\hbar^2}{2m_h^*}\nabla_h^2 - \frac{e^2}{\varepsilon\,|\,r_e - r_h\,|} + \text{polarization term} \quad (1)$$

where the $m^*_e$ and $m^*_h$ are, respectively EM of the electron and hole. To Solving Hamiltonian of clusters for the lowest exited states results[23],

$$\Delta E \cong \frac{\hbar^2\pi^2}{2R^2\mu} - \frac{1.8e^2}{\varepsilon R} + \text{smaller terms} \quad (2)$$

The ΔE represents the difference between bands gap of quantum dot and bulk structure. The first term in eqn. 2 is kinetic energy due to quantum size effect and it can be thought of as the infinite square well contribution to the band gap (μ is effective mass and R is the size of quantum dots). The second term takes into account coulomb interaction effects on the electrons and holes. The numerical factor in this term originates from calculations of wave function overlap integrals. In eqn. 2 one can see that the Coulomb term shifts ΔE to lower energy as $R^{-1}$, while the quantum localization terms shift ΔE to higher energy as $R^{-2}$ so the band gap will always increase for small enough R. The ΔE calculation was performed for ZnS using the following[24]:

Band gap of bulk = 3.84 eV, $\mu = 0.24\ m_e$

where $m_e$ is electron mass. The EMA results for ΔE are compared with the experimental[25] as show in Fig. 1. The results show that there is a good agreement between experiment and effective mass approximation for particle sizes grater than 2.5 Å. The large difference for sizes below 2.5 Å is due to the use EM bulk value of ZnS. Therefore, it is necessary to use the proper EM value to reduce this deference.

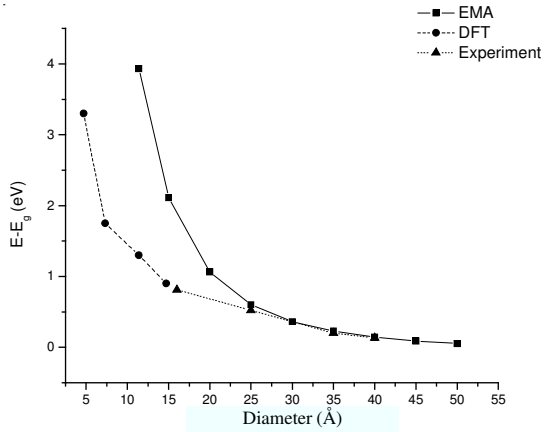


Fig. 1. Continues line is effective mass approximation (EMA) result (eqn. 2), the dot line is experimental result [Ref. 25] and the dash line is DFT approximation (this work)

**Computational method:** The effective mass approximation (EMA) method can not describe the band gap for small size. Therefore, the DFT method was used to obtain the band gap of quantum dots specifically for the ZnS nano particle. In the DFT method, by solving the Kohn-Sham equation and finding the eigenvalue and eigenstate one can find the band gap. For defining the quantum dot system we have used a supper cell surrounded by vacuum in three dimensions. To omit dangling bands of system H-passivation method was used[26].

The structure of ZnS at room temperature is cubic (zinc blende) form, while wurtzite, the less dense hexagonal form, is stable above 1020 °C at atmospheric pressure and metastable as a macroscopic phase under ambient conditions. The relative stability of these phases is modified in both synthetic and natural ZnS nanoparticles[27,28]. Fig. 2 shows structure for ZnS quantum dot that contained 5, 17, 41 and 83 atoms.

The *ab initio* software program espresso was used for calculations, which treats the multi-particle problem of electrons in a period crystal by the density-functional theory (DFT) and using the pseudo-potential method. We used norm conserving

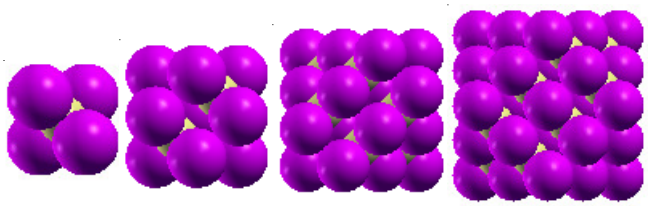

Fig. 2. Geometry of the structure ZnS quantum dot which contain 5, 17, 41 and 83 atoms, respectively

pseudo-potential for nearly exact result respect to soft pseudo-potential. The optimum energy cut off for this pseudo-potential obtain about 100 Ry that is larger than the energy cut off for soft pseudo-potential. This energy cut off increase time of calculation but the result is better and near to experimental data. We can used this software for ZnS quantum dots by choosing a super cell. The optimum length of super cell can be obtained by minimum energy for system. This optimum length is obtained about 10.1 Bohr that is agreement with experimental that is about 10.2 Bohr[29]. Also the optimum cut off is calculated about 30 and 140 Ry for wave function and charge density, respectively.

## RESULTS AND DISCUSSION

The DOS for ZnS quantum dots sizes 0.47, 0.73, 1.14 and 1.47 nm and bulk system are presented in Figs. 3-7. As shown in these figures the shape of DOS for small sizes changed and it looks like a comb. It is also noticed that as the size of the particle decrease, the band gap increase, as a result accident the blue shift, as expected by the theory and experiment.

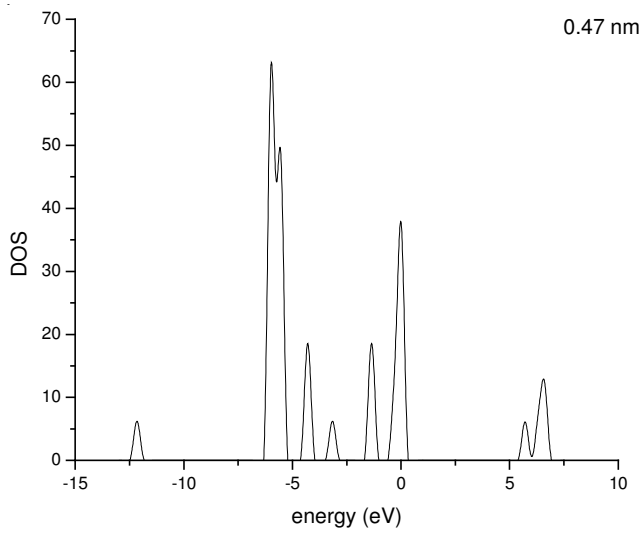


Fig. 3. DOS for ZnS quantum dot with diameter 0.47nm

From the calculation results of DFT and using eqn. 2, it is observed that, as the size of the ZnS nano particles decrease, the EM value will increase. These results are presented in Table-1. Also the results of DFT method are shown in Fig. 1 and compared with experimental and effective mass approximation results. The results show that DFT calculation for quantum dot is good and fit to experiment. Because we solve Hamiltonian of ZnS quantum dot the results are better than the effective mass approximation.

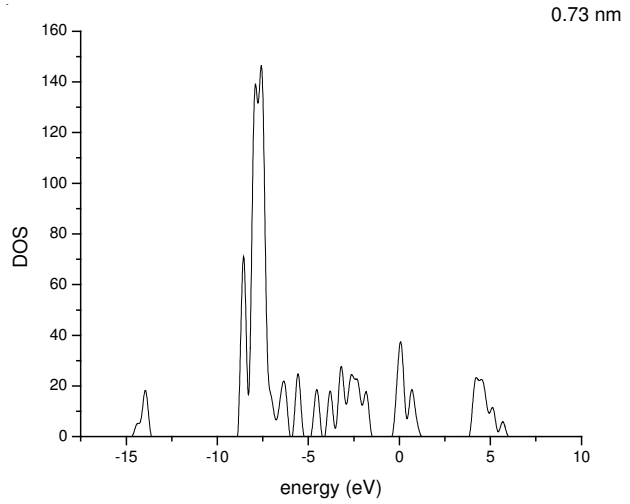


Fig. 4. DOS for ZnS quantum dot with diameter 0.73 nm

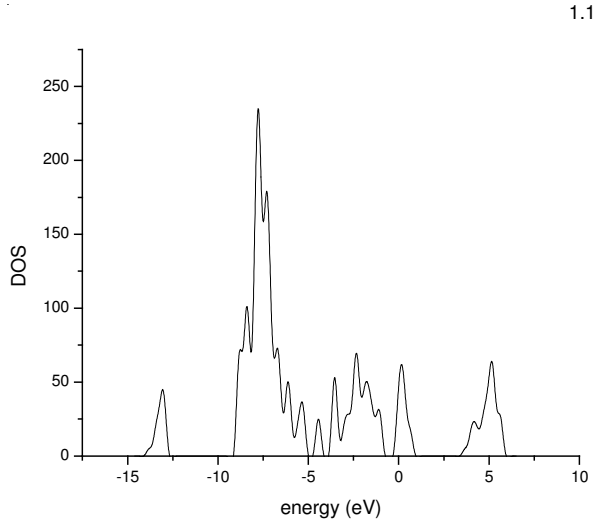


Fig. 5. DOS for ZnS quantum dot with diameter 1.14 nm

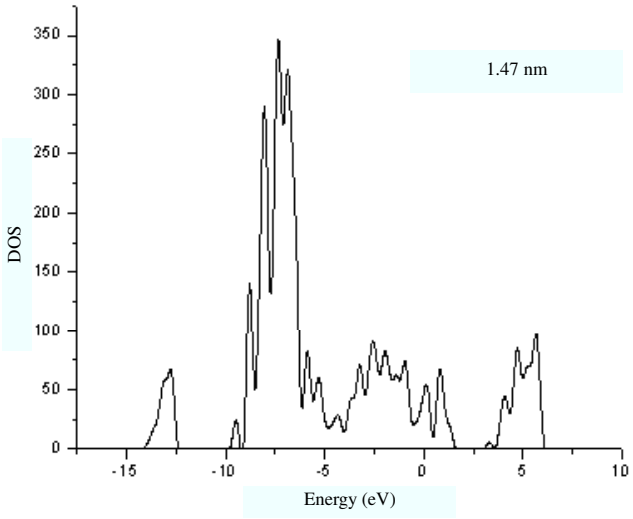


Fig. 6. DOS for ZnS quantum dot with diameter 1.47 nm

By using the results of DFT approximation the changes of the effective mass *versus* the diameter of quantum dot draw in Fig. 8. This figure is show that the effective mass of ZnS quantum dot increase with decrease the size of ZnS quantum dot. The equation that show this variation is

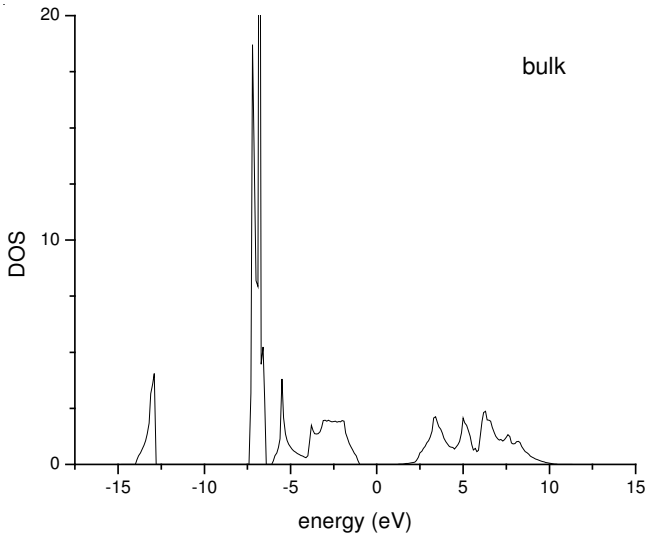


Fig. 7. DOS for ZnS bulk

TABLE-1
ΔE AND EFFECTIVE MASS FOR DIFFERENT SIZES OF ZnS QD BY USING DFT

| Size (nm) | ΔE (eV) | Effective mass ($m_e$) |
|---|---|---|
| Bulk | 0.00 | 0.21 |
| 1.47 | 0.90 | 0.44 |
| 1.14 | 1.30 | 0.53 |
| 0.73 | 1.75 | 0.90 |
| 0.47 | 3.30 | 1.25 |

$$\mu = \left[0.21 + 2.24\exp\left(\frac{-R}{6.09}\right)\right] m_e^* \quad (3)$$

According this equation with increase the R, μ converge to the 0.21 $m_e$ that it is the bulk effective mass ZnS. For larger size of 2.5 nm variation of effective mass for ZnS quantum dot is small and negligible. Therefore if we input the bulk effective mass for the large size of quantum dot the results is in agreement with experiment. But for small size of ZnS quantum dot results isn't correct. If we want to use the eqn. 2 we must input the correct effective mass.

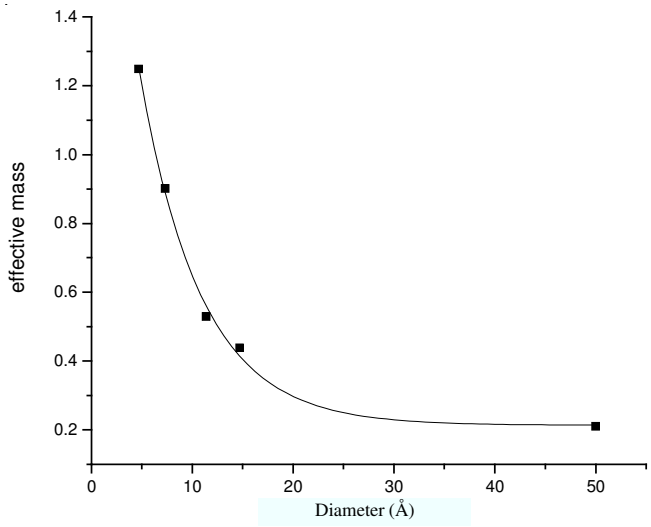


Fig. 8. Effective mass approximation as a diameter of ZnS quantum dots

We input eqn. 3 in eqn. 2 and derive new equation and calculate variation of energy for different size of ZnS quantum dot. The results of new method for effective mass approximation is shown in Fig. 9 and compared with old effective mass approximation and experimental results. This new effective mass approximation acquired with experimental result.

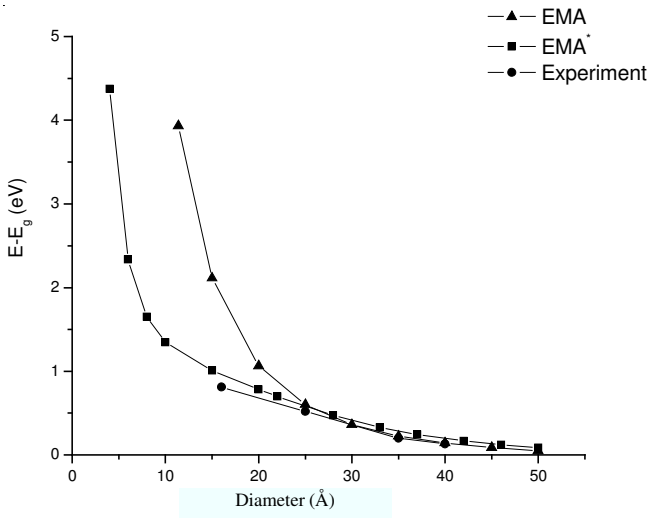


Fig. 9. Triangle is EMA, the square is new EMA and the circle is experimental results

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